Influence of Mechanical Stresses on the Hydrolytic Aging of Standard and Low Styrene Unsaturated Polyester Composites

M. AUTRAN,[1] R. PAULIARD,[1] L. GAUTIER,[1] B. MORTAIGNE,[2] F. MAZEAS,[3] P. DAVIES[3]

[1] DGA/Centre Technique d'Arcueil, 16 bis, avenue Prieur de la Côte d'Or, 94114 Arcueil Cedex, France

[2] DGA/SPAé/ST/CEA, 26 Boulevard Victor, 75015 Paris, France

[3] Ifremer/Centre de Brest, BP70, 29280 Plouzané, France

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ABSTRACT: Standard and low styrene emission glass fiber-reinforced unsaturated polyester (FRP) composites were aged by immersion under flexural and tension loads, to evaluate modifications to the mechanical properties as a function of exposure time under stress. The application of a mechanical load does not modify either the quantity of the absorbed water or the diffusion coefficients significantly. For an applied stress of less than 10% of the fiber strength, the influence on aging is small, but for larger applied stresses, the rate of reduction in the mechanical properties is accelerated and, in some cases, premature rupture is observed. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 2185–2195, 2002

Key words: unsaturated polyester–glass-fiber composites; mechanical properties; water diffusion; aging; aging under load

INTRODUCTION

One of the major limitations to the development of polymers and composites is the lack of knowledge of their long-term behavior. The development of certification methods for the suitability of composite materials for specific functions requires not only an improved understanding of degradation mechanisms, but also an approach linked to mechanical property evolution,[1–4] as these two components determine the material lifetime.

Composite materials, with an unsaturated polyester matrix and glass-fiber reinforcement, find many applications in naval structures. These composites hold a particular interest as they have the ability to be made into large structures (without high-temperature cure) at low cost. Technological and economic evolutions are leading to a growing interest in the improvement of the durability of these materials under service conditions.[5,6] Unfortunately, it has been shown that glass polyester composites are sensitive to hydrolysis due to the presence of hydrolyzable ester functions in their structure, and they degrade by osmotic cracking. This hydrolysis is proportional to both the amount of water introduced in the polymer and to the chain-end concentration in the network.[7,8] The influence of acidic and alcohol constituents on the rate of ester function hydro-

Correspondence to: B. Mortaigne.

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lysis was also determined recently with accuracy.[9,10]

Regarding the fabrication of these composites, it is necessary to emphasize the importance of changes in environmental safety laws for the use of organic products. In the case of glass-fiber/polyester (FRP) composites, lower allowable styrene emission levels have resulted in much research into materials with little or no styrene emission. These new resins will need to be certified for long-term use by taking into account the mechanical loads (aging under stress, pressure, etc.) and chemical reactions (humidity, temperature, etc.) which will be encountered in service. Matrix resins with dicyclopentadiene (DCPD) chain ends are one of the solutions proposed, which reduce styrene emission during manufacture by modification of the chemical prepolymer structure. It has been shown that the chemical structures of the networks obtained after polymerization, and therefore the hydrolysis mechanisms, are not greatly modified by the presence of these DCPD chemical groups at the chain ends. Nevertheless, these resins are more sensitive to hydrolysis than are traditional unsaturated polyester resins[11] due to their low molecular weight and to the prepolymer chemical composition that contains easily hydrolyzable ester functions.[12]

By coupling physicochemical results with studies of the mechanical and micromechanical property evolution of these FRP composites, their mechanisms of osmotic damage have been examined in detail.[13,14] It was shown that the induction time for microcracking could be used as a relevant criterion for lifetime estimation. Mechanical tests on composites enable rules to be defined for the estimation of their long-term behavior by using time–temperature superposition diagrams.

The addition of load to moisture at elevated temperature during conditioning was studied in some detail in previous work on stress corrosion cracking in the 1980s.[15–18] However, this aspect of the behavior of low styrene emission resins has received very little attention to date. Numerous researchers have already explored the combined effects of moisture and elevated temperature exposure on the durability of polymeric composite materials and Weitsman reviewed the literature in this area recently.[19] However, since these composites are currently used in, or are intended for, structural applications, it is necessary to be able to predict their performance under load in severe environments.

In this article, the influence of a mechanical load on the aging behavior of standard and low styrene emission FRP composites was examined. This includes a study on water-sorption kinetics and analysis of the evolution of mechanical properties of composites aged under flexural and tension mechanical loading.

EXPERIMENTAL

Materials

Two polyester resins were tested, both provided by the Cray Valley Total Co. (France):

- A traditional resin (G703) composed of isophthalic acid, maleic acid, and propylene glycol in molar proportions of 0.5/0.5/1, respectively, with a styrene ratio of 45 wt % and considered as a high styrene emission resin;
- A low styrene emission resin with DCPD chain ends (Enydyne), composed of orthophthalic acid, maleic acid, and propylene glycol, together with ethylene glycol, diethylene glycol, and DCPD in molar proportions of 1.1/2/0.55/1.7/0.56/1, respectively, with a styrene ratio of 40 wt %.

The reinforcement was a 545 g/m^2 E-glass taffeta weave (RT500 from the Vetrotex Co., France), which is based on glass fibers with a mean diameter of 18 $\pm$ 2 μm and P 177 sizing. Before use, cloths were dried for 24 h at 70°C. Polymerization of these resins involves addition of 0.5 wt % of a cobalt octoate solution (NL51, Akzo) as a catalyst and 1.5 wt % of a methyl ethyl ketone peroxide solution (Butanox M50, Akzo, France) as an initiator. Composites were made by impregnating six layers of reinforcement cloth. The six plies were all laid up in the same orientation. The composites were processed in a compression press. They were cured for 24 h at room temperature, then with a cycle of 10 h at 80°C, followed by 4 h at 120°C.

The composites' T_g's were determined on a Metravib thermomechanical spectrometer (maximum of the tan δ curve) in torsion, on 70 $\times$ 10 $\times$ 2-mm dimension specimens, with an increased temperature rate of 1°C/min. G703/P177 and Enydyne/P177 composites have glass transition temperatures of 110 $\pm$ 2°C and 81 $\pm$ 2°C, respectively. The fiber ratio, obtained by total combustion of an organic compound under air in an oven

Table I Initial Mechanical Characteristics

Flexure	Flexural modulus (MPa)	Ultimate Flexural Strength (MPa)
G703/P177	16,050 ± 2.30	468 ± 35
Enydyne/P177	15,700 ± 400	492 ± 50

Tension	Ultimate Tension Strength (MPa)	Ultimate Tension Strain (%)	Tension Modulus (GPa)	Knee Value (MPa)	Knee Value (%)
G703/P177	274 ± 13	2.22 ± 0.1	15.6 ± 0.4	76 ± 5	0.47 ± 0.03
Enydyne/P177	265 ± 15	2.54 ± 0.1	14.4 ± 0.5	68 ± 5	0.48 ± 0.05

at a temperature near 550°C, was 64 ± 1 wt % for each composite panel, and the void ratio in the two materials was around 2 ± 0.5 vol %. The ratio of the void was calculated using the density of E-glass and the density of the unsaturated polyester network measured on neat materials.

Water Sorption

Water-sorption tests and the aging of composites were performed by immersion in distilled water at three temperatures: 30, 50, and 70 ± 2°C. The bath-immersion temperature was regulated using a heating electronic thermometer.

Aging in Flex

Specimens of dimensions of 80 × 15 × 3 mm^3 were loaded in a three-point bending mechanical test. The distance between the external bars was 48 mm and the outer loading axes had a diameter of 4 mm, while the central axis had a 10-mm diameter. In the test configuration, specimens were loaded with an imposed displacement. The applied mechanical load was determined from the initial stress/strain curve in flexure of the composite. The applied bending stresses at the center of the specimen correspond to displacements of 0.5, 1, and 2 mm and to static loads of 12, 25, and 50% of the ultimate flexural strength. After aging, wet specimens were characterized by three-point bending tests.

Aging in Tension

The two types of composites were immersed for 3 months (90 days) in distilled water at 50 ± 2°C, with different applied loads. The specimen dimensions were 800 × 25 × 3 mm. The tensions applied during immersion were determined by applying a percentage of the ultimate strengths obtained from the tensile stress/strain curve for dry, unaged composites. This load was applied by suspending dead weights. After immersion, specimens were cut into bars of 250 × 25 × 3 mm so that only three tests could be performed for each immersion condition. Hence, it is difficult to give a statistical interpretation of the results, because we did not have enough mechanical test machines to expose more specimens for such a long time, but the obtained results seem to be consistent.

Determination of Mechanical Properties

Initial flexural and tension mechanical characteristics were obtained by testing 10 specimens of each composite.

Flex

Mechanical tests in three-point bending were performed on an Instron 6025 test machine. Tests were conducted at room temperature on specimens with 80 × 15 × 3-mm dimensions. The distance between supports was 48 mm, and the crosshead displacement speed was 2 mm/min. This experimental part was in accordance with the NF T 51 001 procedure.

Tension

Tensile tests were carried out on an Instron 6025 test machine with a typically used crosshead displacement speed of 2 mm/min. Tests were performed at room temperature. Specimen dimensions were 250 × 25 × 3 mm.

RESULTS AND DISCUSSION

Initial Properties

The initial mechanical properties obtained in flex and in tension for the two FRP materials are

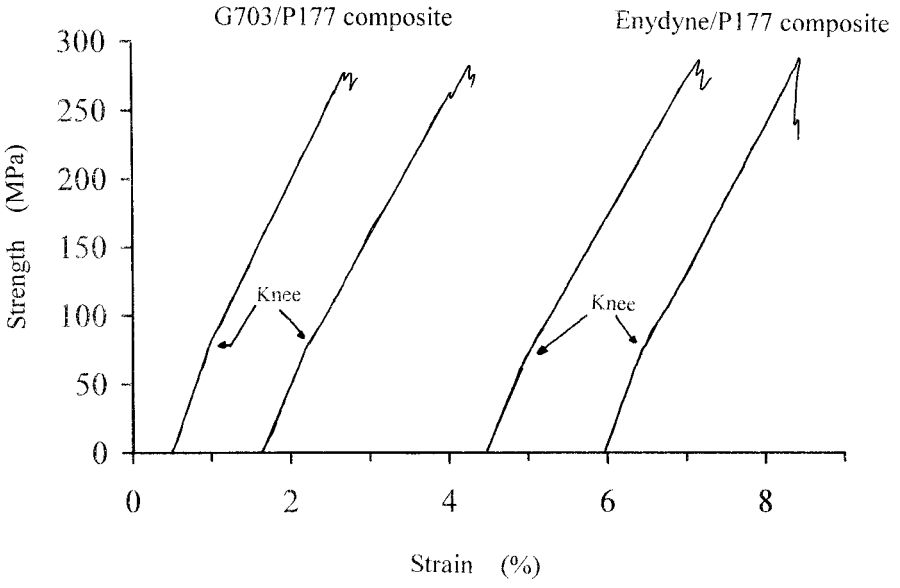

Figure 1 Tensile mechanical test curves of G703/P177 and Enydyne/P177 composites.

listed in Table I. The failure mode was brittle, as we can see in Figure 1. These stress/strain results were used to determine loading conditions for the aging tests.

In tension, the ultimate strain was higher for Enydyne than for G703 and the modulus was a little lower. This may be related to the lower prepolymer molecular weight of the former, which was observed to result in a lower glass transition temperature for Enydyne, 81°C instead of 110°C for the G703 resin. Looking more closely at the stress/strain curves, we observed an initial linear part of the curve, followed by a "knee." Several authors used nondestructive tests such as acoustic emission (AE) to explain damage mechanisms which occur during mechanical tests on composites, and this knee has been shown to correspond to matrix cracking initiated by 90° reinforcement.[15,16]

Water Sorption

Table II shows the average equilibrium water concentrations and the diffusion coefficients of the two FRP materials. Concerning the equilibrium water concentration (W_{eq}), there is not a significant influence of the applied flexural load on the weight gain of either material, except for a load of 50% of the ultimate flexural strength. In this case, it seems that the materials do absorb a

Table II Equilibrium Water Concentrations (W_{eq}) and Diffusion Coefficients (D) of G703/P177 and Enydyne/P177 Composites

		Flexural Stress Applied (as Fraction of the Ultimate Flexural Strength Value)							
		0%		12%		25%		50%	
Composite	Temperature (°C)	W_{eq}	D (cm^2,s^{-1})	W_{eq}	D (cm^2,s^{-1})	W_{eq}	D (cm^2,s^{-1})	W_{eq}	D (cm^2,s^{-1})
G703/P177	30	0.17	$14.E^{-9}$	0.25	$9.E^{-9}$	0.25	$31.E^{-9}$	0.30	$34.E^{-9}$
	50	0.30	$22.E^{-9}$	0.30	$24.E^{-9}$	0.35	$25.E^{-9}$	0.40	$23.E^{-9}$
	70	0.40	$67.E^{-9}$	0.37	$64.E^{-9}$	0.40	$67.E^{-9}$	0.27*	$54.E^{-9}$
Enydyne/P177	30	0.30	$8.E^{-9}$	0.30	$6.E^{-9}$	0.30	$15.E^{-9}$	0.35	$25.E^{-9}$
	50	0.47	$20.E^{-9}$	0.42	$25.E^{-9}$	0.50	$20.E^{-9}$	0.60	$19.E^{-9}$
	70	0.65	$58.E^{-9}$	0.75	$44.E^{-9}$	0.80	$38.E^{-9}$	0.95	$53.E^{-9}$

little, but significant, more water, except in the case of the G703/P177 composite in water immersion at 70°C, where the absorbed water amount is lower. We have no explanation for this result, the test being performed at a temperature far from the material glass temperature even if it is in a humid state ($T_{g_{humid}} \approx 105$°C).

As was already observed in previous work,[7] W_{eq} levels are higher when the temperature is increased, and materials with the Enydyne matrix absorb more water than do materials with the G703 matrix due to the more hydrophilic nature of its prepolymer structure.[11] The equilibrium plateau is reached more rapidly when the temperature is higher, always staying at a temperature lower than the T_g with the polyester in a glassy state.

When we plot the water amount absorbed versus the square root of the time, the beginning of the curve obtained is a straight line. An example of these curves, for the composites aged in water at 50°C, is shown in Figure 2. This allows water-diffusion coefficients (D) to be determined for the composites using Fick's law as a first approximation, even though composites are inhomogeneous by definition. D increases with the temperature and is not very different for the two materials studied here. Concerning the diffusion coefficient values (D) obtained with a high flexural strength (25 and 50%) at 50°C, we have no easy explanation for the low values determined.

We also observed that the rate of the flexural mechanical load applied does not seem to have a very high impact on the water-sorption rate. If we examine more closely the curves of the sample weight variation with time, we observe that

- At 30°C, the saturation plateau appears after approximately 300 h for the two materials, and a weight decrease can be detected in the case of Enydyne composites after this duration;
- At 50°C, the saturation plateau appears after approximately 200 h, for the two composites, and then we observe weight decreases corresponding to hydrolysis of the polyester system with extraction of small molecules, as was noted in previous tests on materials not reinforced by fibers.[8,12]
- At 70°C, the saturation plateau can be localized between 100 and 150 h for the two materials. Subsequently, an extraction phenomenon occurs involving hydrolyzed and extracted molecules compensated by a phenomenon of increasing network hydrophilic behavior. This latter increase corresponds to a rapid hydrolysis rate of ester functions together with fiber/matrix interface phenomena.

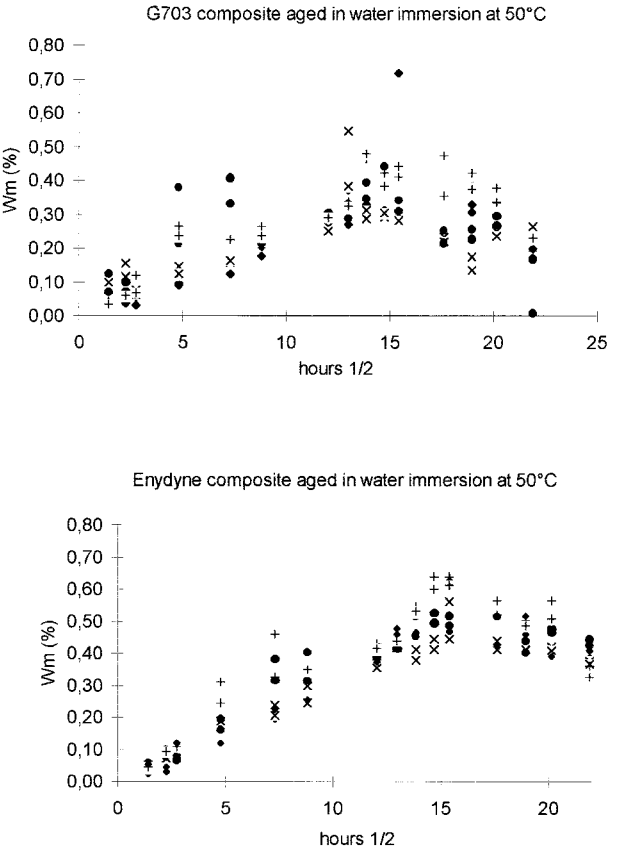

Figure 2 Water-sorption curves of G703/P177 and Enydyne/P177 composites in immersion at 50°C under different flexural load levels: (♦) without load (×) 12% flexural strength; (●) 25% strength + 50% strength.

During immersion, temperature and humidity induce a differential stress at the fiber/matrix interface, resulting from differential expansion of the glass fiber and the matrix. Previous work on the artificial aging of FRP composites, particularly studies on single glass fibers, showed that fracture is produced by a complex multiaxial load and occurs before the matrix is highly degraded.[1] These phenomena help to explain the high levels of water observed in composites after the matrix resins have reached saturation.

Aging with Tension

Tables III and IV show results from tests in tension on specimens which have been aged in water

Table III Tensile Properties of G703/P177 Composites After 90 Days of Immersion in Water at 50°C for Different Mechanical Loads

Applied Strength in Tension (%)	Ultimate Tension Strength (MPa)		Ultimate Tension Strain (%)		Tension Modulus (GPa)		Knee (MPa)	Knee (%)
	Value	Average	Value	Average	Value	Average		
0	212	200	1.68	1.57	15.9	15.9	74.4	0.50
0	190		1.48		16		86.3	0.54
0	199		1.54		15.7		90.1	0.56
14	184	193	1.34	1.39	16.8	17.2	86.5	0.50
14	202		1.44		17.5		79.6	0.49
23	197	209	1.38	1.49	15.9	17.4	79.0	0.46
23	221		1.56		17.8		78.6	0.42
23	209		1.54		18.5		82.7	0.49
28	200	202	1.46	1.34	14.9	15.1	85.2	0.56
28	205		1.14		15.9		78.7	0.44
28	180		1.42		14.6		74.6	0.47
33	197	199	1.50	1.44	14.9	15.6	69.4	0.45
33	205		1.48		15.9		88.4	0.56
33	194		1.34		15.9		68.5	0.40

at 50°C for 90 days (2160 h). After 90 days of exposure at 50°C, the applied tension load does not seem to affect either the ultimate tensile strength of the composite or the tensile modulus value. The combination of stress and water did not induce much stress cracking in the glass fibers, as was obseved in some experiments.[15–18] Only in the case of an applied load level of 23% did tension strain and modulus values increase, while strain at break decreased. Apart from this case, whatever the load applied, an identical value for the strain at break of approximately a value of 1.40% was obtained. Concerning the knee detected on the tension curve, a point attributed to the beginning of microcracking in the composite,[20,21] this always appears at a tensile stress level of 80 MPa, but with a strain a little lower for the higher applied external load. By comparing the mechanical characteristics of samples aged without load with the initial mechanical characteristics of the composite (see Table I), it may be noted that the ultimate tensile strength as well as the ultimate tensile strain are much lower. The absorbed water, by modifying the glass matrix interface, resulted in values reduced by around 30% with respect to their initial value.

Water in composites modifies the effective free volume in resins, which explains the changes recorded for the glass transition temperatures (T_g's).[22] Physical and chemical aging phenomena resulting from water exposure are highly accelerated by the presence of fibers. Water modifies composite and network properties in preferential directions, and it can cause plasticization and fiber/matrix debonding.[23,24] In the case of the Enydyne/P177 composite, when the applied tension stress increases, the tension modulus decreases greatly while the ultimate tension strength and the ultimate tension strain decrease in a similar manner. During aging, hydrolysis cuts molecular chains of the network, which induces a decrease in the mechanical properties. As the test is conducted on imposed load conditions, in some regions of the specimen, the imposed load becomes very quickly superior to the ultimate mechanical properties of the material, and the specimen breaks.

For the G703/P177 composite, the influence of humidity on the initial properties is lower (decreases 6–10%) but hydrolysis and interface water-sorption phenomena are very important. These results are similar to those obtained by Chiou et al.[21] in the case of composite tubes tested under load, where it was shown that the combination of water and mechanical load caused a reduction in the time to reach failure.

Comparison with Dry Tests

To separate the influence of humidity from the influence of the applied load, composite speci-

Table IV Tension Properties of Enydyne/P177 Composite After 90 Days of Water Immersion at 50°C Under Mechanical Loading

Applied Strength in Tension (%)	Ultimate Tension Strength (MPa)		Ultimate Tension Strain (%)		Tension Modulus (GPa)		Knee (MPa)	Knee (%)
	Value	Average	Value	Average	Value	Average		
0	239	235	2.37	2.39	14.6	14.3	47.3	0.40
0	232		2.21		13.7		53.4	0.45
0	233		2.59		14.6		49.8	0.42
14	237	242	2.19	2.33	11.9	13.8	67	0.51
14	247		2.42		13.9		69	0.52
14	241		2.37		13.8		61	0.47
16.5	231	232	2.28	2.18	13.4	13.6	62.9	0.46
16.5	239		2.08		13.9		54.1	0.36
16.5	225		2.19		13.6		53.6	0.37
23	210	228	1.91	2.10	12.5	13.2	55.4	0.46
23	240		2.18		13.7		63	0.44
23	235		2.21		13.3		53.3	0.37
28	216	219	1.89	1.90	13.8	13.7	58	0.38
28	224		1.91		13.4		50	0.35
28	218		1.89		13.4		57	0.40
33	201	211	2.08	−2.12	12.0	12.4	53.1	0.47
33	227		2.27		13.0		59.3	0.51
33	206		2.01		12.1		66.6	0.53

Note that for Enydyne three specimens broke prematurely: after 15 days for a sample loaded at 33% of the ultimate strength, after 20 days for a sample loaded at 28% of the ultimate strength, and after 80 days for a sample loaded at 33% of the ultimate strength. Nevertheless, all mechanical tests were performed after immersion in water for 90 days.

mens were subjected to a tension load of 28% of the ultimate tension strength but maintained in conditions of ambient temperature and humidity (23°C, 70% RH). The tests were performed during a relatively long time, so only three specimens of each material were tested, which only allowed us to make qualitative observations to obtain evolutionary trends and did not allow us to make a statistical analysis. The results are shown in Table V.

For G703/P177 composites, tension load does not seem to influence either the strength or the

Table V Mechanical Characteristics of Composites Aged for 90 Days at Ambient Temperature and Humidity Under a Tensile Load of 28% of the Ultimate Tensile Strength

Applied Strength in Tension (%)	Ultimate Tension Strength (MPa)		Ultimate Tension Strain (%)		Tension Modulus (GPa)		Knee (MPa)	Knee (%)
	Value	Average	Value	Average	Value	Average		
G703/P177								
0		274 ± 13		2.22 ± 0.1		15.6 ± 0.4	76 ± 5	0.47 ± 0.03
28	284	271	2.42		16.9		98	0.56
28	258		1.96	2.17	16.6	16.8	103.4	0.63
28	271		2.12		16.9		103.9	0.62
Enydyne/P177								
0		265 ± 15		2.54 ± 0.1		14.4 ± 0.5	76 ± 5	0.47 ± 0.03
28	256		2.11		15.6		82	0.53
28	267	259	2.34	2.27	15.1	15.1	102	0.75
28	254		2.38		14.5		85	0.59

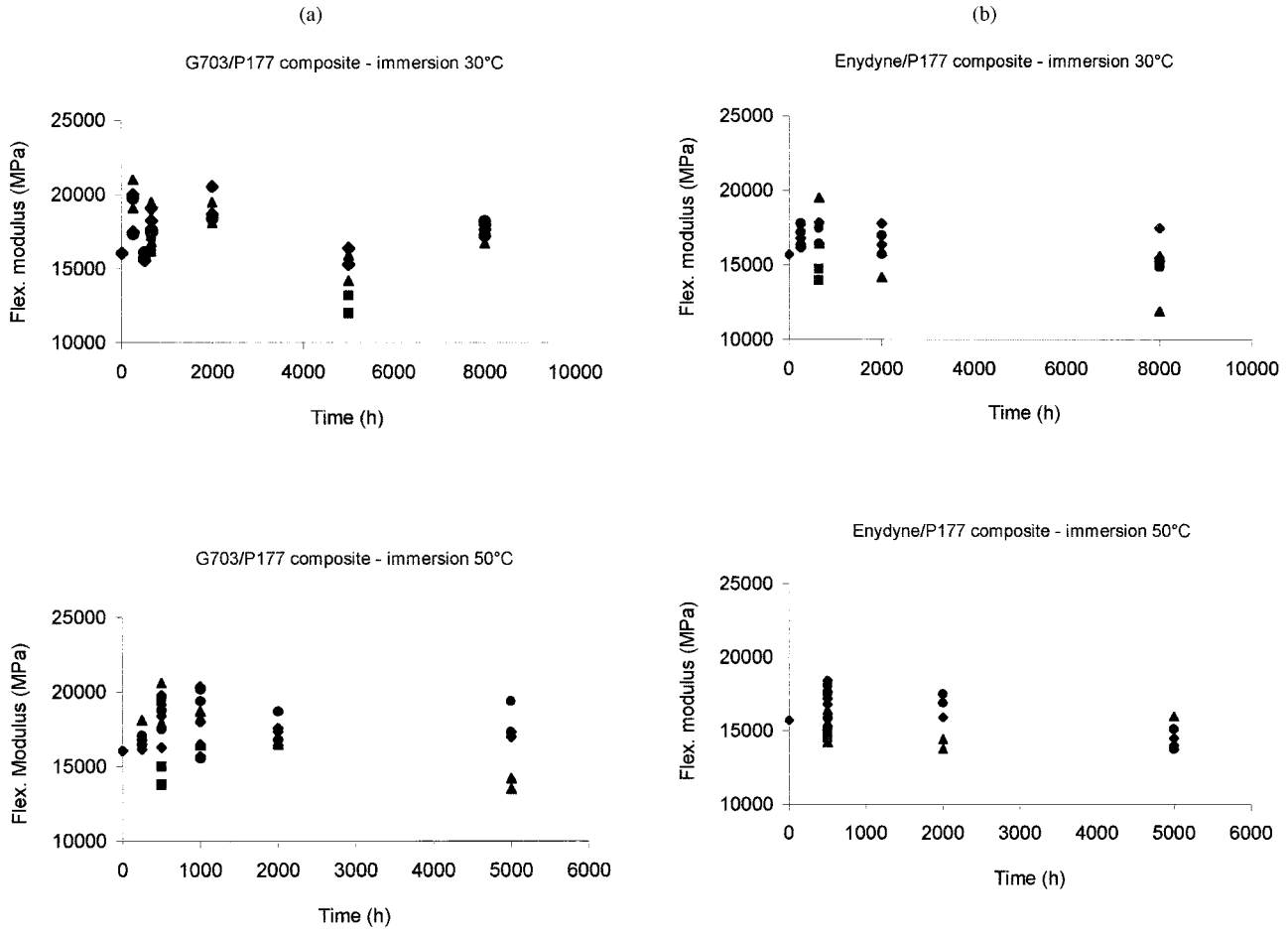

Figure 3 Evolution of flexural modulus, in immersion at 30 and 50°C, under different flexural load levels. (♦) Without load; (●) 12% flexural strength; (▲) 25% flexural strength; (■) 50% flexural strength: (a) for G703/P177 composites; (b) for Enydyne/P177 composites.

strain at break of the composites, and the tension modulus even increased. For the Enydyne/P177 composite, the ultimate tensile strength is constant but the ultimate tension strain is slightly reduced. For the two materials, the modulus in tensile increased by 1 GPa. Similarly, the knee on the stress/strain curve, corresponding to the beginning of microcracking, was offset to higher values of stress and strain.

It may be that during aging the matrix creep reorients fibers in the tension axis, which increases the modulus. No physical aging of the matrix has been noticed. On the other hand, this creep can lead to premature failure. This is particularly true for the Enydyne composite system formed by the crosslinking of short prepolymer chains that very often have only one crosslinking point in their structure.[13]

Aging in Flex

In the case of a structural composite, aging under flex corresponds to a more realistic loading than does aging in tension. In this type of loading, the lower face is subjected to stresses in tension, while the upper face is loaded in compression. Modes of rupture such as the cracking of the matrix, debonding of the fibers, and fiber fracture may occur in tension, in compression, in shear, or by a combination of these different stresses.[25] It is known, in this case, that water swelling of the polyester induces fiber compression[26] that could increase the mechanical properties under stress.

In Figure 3(a,b), the evolution of the flexural modulus for the two composites during water immersion at 30 and 50°C is shown. This modulus decreases during aging and the loss of property is

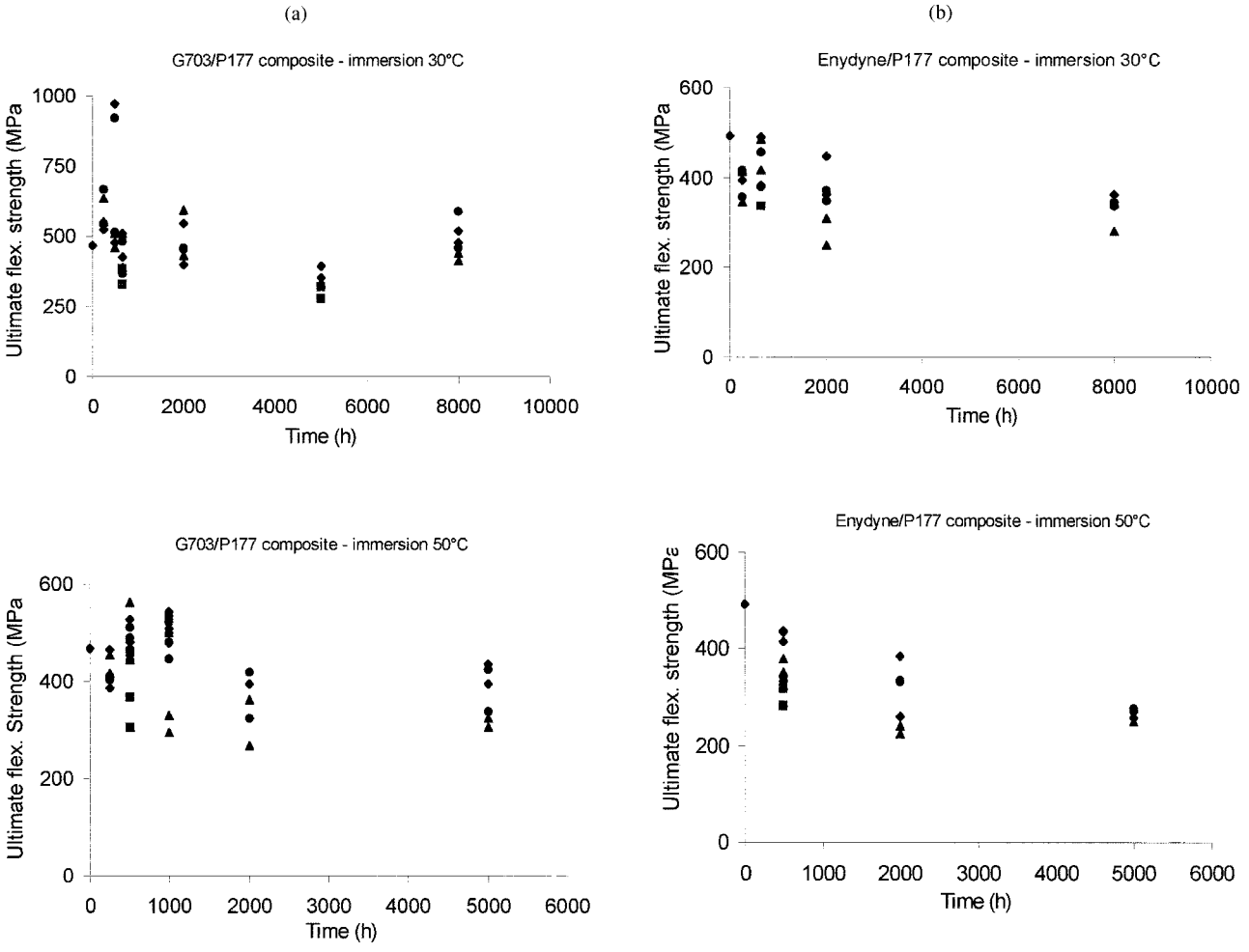

Figure 4 Evolution of ultimate flexural strength in immersion at 30 and 50°C under different flexural load levels. (♦) Without flexural load; (●) 12% flexural strength; (▲) 25% flexural strength; (■) 50% flexural strength: (a) for G703/P177 composites; (b) for Enydyne/P177 composites.

more important when the applied load level is higher. Knowing from previous results that the flexural and tensile moduli of an unsaturated polyester matrix decrease very little during aging, the decrease observed here may be explained by the loss of cohesion between the matrix and the glass fibers.

At 30 and 50°C, temperatures that are distant from the materials' T_g's, even in the wet state, with or without a 12% load, the flexural modulus loss is low, but becomes important as soon as the applied stress reaches 25% of the ultimate value. This loss of modulus is greater with Enydyne composites than for those based on G703 resin, but the temperature test in the Enydyne case is much closer to the T_g. In the case of the Enydyne material, a load less than 12% does not seem to have any influence; for the G703 composite, it would seem that a flexural stress of 12% improves aging resistance.

Figure 4(a,b) shows the ultimate flexural strength for the two composites during water immersion at 30 and 50°C. A reduction in values is apparent. For applied flexural loads corresponding to 25 and 50% of the ultimate strength, the loss of properties becomes important very quickly and is greater at higher applied loads. This test is complex, but from the results described above, it is apparent that the tension effect is small, so that it is either the shear or compression component that limits the composite's aging stability. The observation of specimen delamination suggests that it may be interlaminar shear which dominates. The interlaminar shear properties are de-

Table VI Mechanical Characteristics of Composites Aged in Flex in Immersion at 70°C for 300 h

Composite	Time (h)	Flexural Modulus (MPa)	Ultimate Flexural Strength (MPa)
G703 70°C	Initial	16,050	468
Bending load 0 mm	300	18,700	392
Bending load 0 mm	300	16,100	349
Bending load 0.5 mm (12%)	300	16,100	342
Bending load 0.5 mm (12%)	300	19,500	347
Bending load 1 mm (25%)	300	15,900	276
Bending load 1 mm (25%)	300	16,500	330
Bending load 2 mm (50%)	300	15,100	289
Bending load 2 mm (50%)	300	19,000	362
Enydyne 70°C	Initial	15,700	492
Bending load 0 mm	300	17,500	220
Bending load 0 mm	300	17,100	342
Bending load 0.5 mm (12%)	300	15,850	281
Bending load 0.5 mm (12%)	300	16,150	270
Bending load 1 mm (25%)	300	16,800	Plasticization
Bending load 1 mm (25%)	300	16,800	Plasticization
Bending load 2 mm (50%)	300	14,250	Plasticization
Bending load 2 mm (50%)	300	14,000	Plasticization

pendent on the matrix and interfacial properties, while fiber properties dominate the composite's behavior in tension.[27] The environmental conditioning weakens interfaces both between plies and between the matrix and fibers in a given ply.[28]

Data obtained from wet aging at 70°C for 300 h are given in Table VI. After this period, the composites are saturated with water. If we refer to the water-sorption curves, the G703/P177 composite contains approximately 0.5 wt % water while the Enydyne/P177 composite contains more than 1 wt % of sorbed water. For conditions of aging at 7°C, we note that after 300 h the Enydyne is no longer brittle but shows matrix plasticization, so the failure mode of the composite is different. At this temperature, the material is close to its glass transition temperature (81°C for the material in a dry state, near 75°C in wet state) and shows a permanent deformation. If we refer to curves of weight variation, we note that at 70°C, after 300 h, Enydyne is already highly hydrolyzed, which also explains this change in the failure mode. For experiments at 30 and 50°C, we observe a reduction in the modulus and the strength with aging, and this loss of properties increases as the applied stress increases.

CONCLUSIONS

Combined effects of water and mechanical stresses on FRP composites were studied for three load levels applied either in tension or in flex. These experiments show

- A mechanical load applied in flex does not modify the amount of absorbed water by the composites, except when the load is 50% of the ultimate strength. This result is very important because it has been shown that the hydrolysis rate of unsaturated polyester resins directly depends on the amount of water in the material. So, an external mechanical load does not modify the hydrolysis kinetics of the FRP composite. Concerning water-diffusion coefficients, these are not appreciably modified by loading in flex or tension. Nevertheless, the water sorption by the composite leads to fiber/matrix debonding that induces a rapid water uptake. This water sorption is more rapid when the temperature is increased.
- Mechanical tests in tension indicate, for the G703 traditional unsaturated polyester resin studied, a negligible effect of the applied load on the evolution of the elastic modulus and the ultimate strength. However, there is an influence on the composite strain at failure. For the Enydyne FRP composite, a reduction in the modulus, strength, and strain at break is noted and these reductions increase as the applied external stress is increased. This second material, which shows a higher interface sensitivity, fails prematurely when it is sub-

jected to external mechanical stress. Combined effects of the temperature, humidity, and mechanical loading decrease the mechanical properties. Ultimate mechanical properties of composites aged without loading are higher than are those of composites aged under stress.

- Aging under flexural loading superior to 12% of the ultimate strength results in a decrease in the flexural modulus and strength. The reduction in these properties is higher for Enydyne than for the G703 composites.

For an applied load near the value of 12% of the strength at break, in the case of G703 FRP, the ultimate strength of the composite is improved. When too much water is absorbed by the composite, a change in the failure mode from brittle to more ductile is noted. Composite damage mechanisms include delamination and fiber–matrix debonding, with the resistance in shear limiting the lifetime of the FRP composite.

The combination of a mechanical load and hydrothermal aging may limit the lifetime of composites, but the influence of this load is highly dependent on the material. In the case of unsaturated polyesters, it has been shown that mechanical stress has a more important effect on the low styrene emission resin Enydyne than on the G703 resin. This difference is directly connected to the structure of the Enydyne matrix, which involves small prepolymer chains with a small number of crosslinking points that produce a material with a low glass transition temperature (81°C for Enydyne in place of 110°C for the G703 composite).

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